Current Status of EBC Exposures in ORNL's Keiser Rigs

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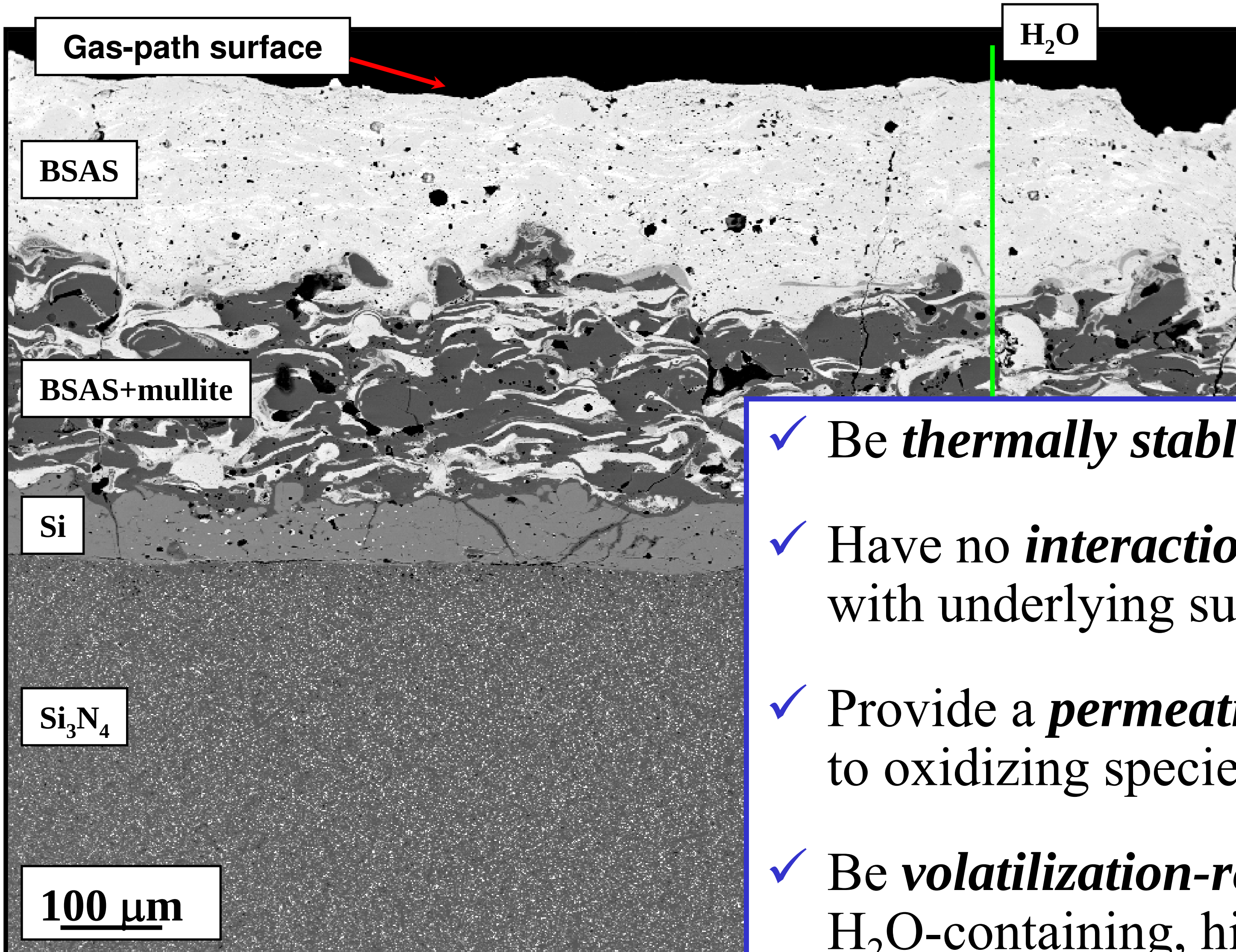
Environmental Barrier Coating Workshop 2005

November 15, 2005

Distributed Energy Program
Office of Energy Efficiency and Renewable Energy

To Effectively Protect A Substrate At High Water-Vapor Pressures, An EBC Must:



- ✓ Be ***thermally stable*** at 1100°C
- ✓ Have no ***interactions/reactions*** with underlying substrate
- ✓ Provide a ***permeation barrier*** to oxidizing species
- ✓ Be ***volatilization-resistant*** in H_2O-containing, high-velocity gas turbine environment

To Assess These Attributes For A Candidate EBC Composition, We Have Used Two Evaluation Modes

- Thermal stability
- Possible interactions with substrate
- Ability to function as a permeation barrier to oxidizing species

→ 10 atm total pressure
1-2 atm H_2O

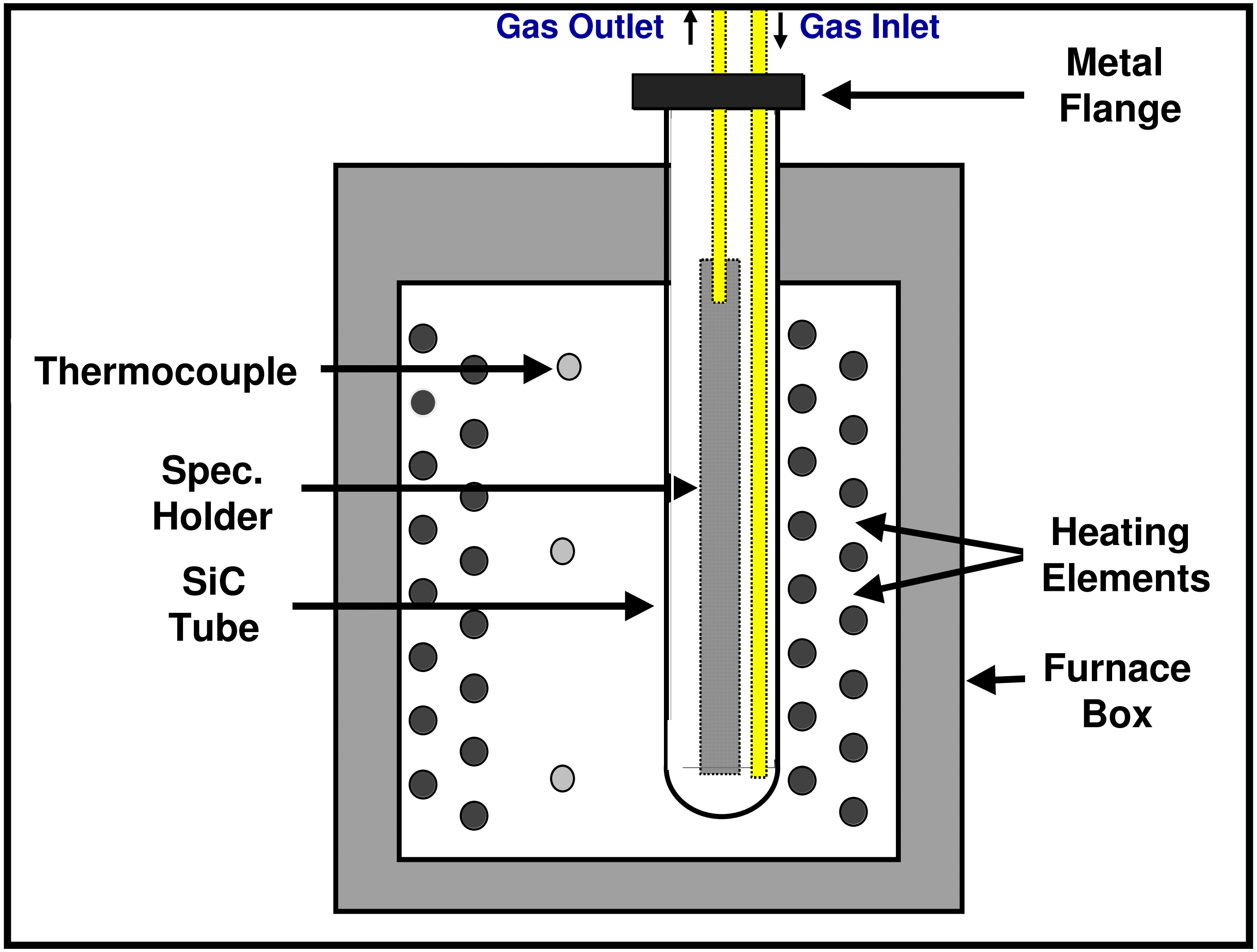
- Volatilization resistance → 20 atm total pressure
~18 atm H_2O

We Ran Exposures In Both Modes In Past Year, Emphasis On Volatilization Resistance

Keiser Rigs Are Used For Both Types Of Experiments

- 1200-1315°C
- Up to 20 atm total pressure
- Air+3-20%H_2O
- 0.05-0.3 cm/s

Schematic of Keiser Rig



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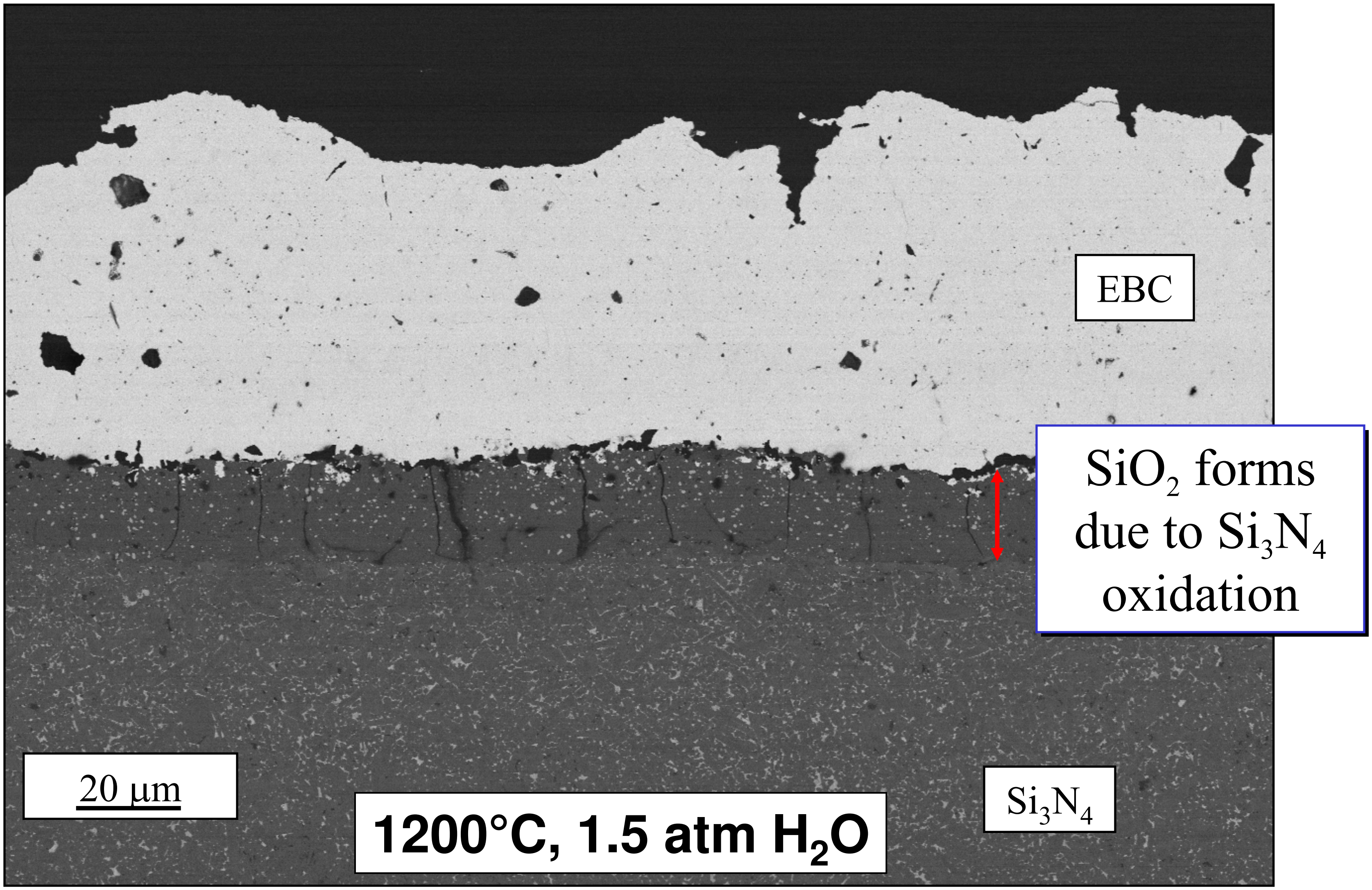
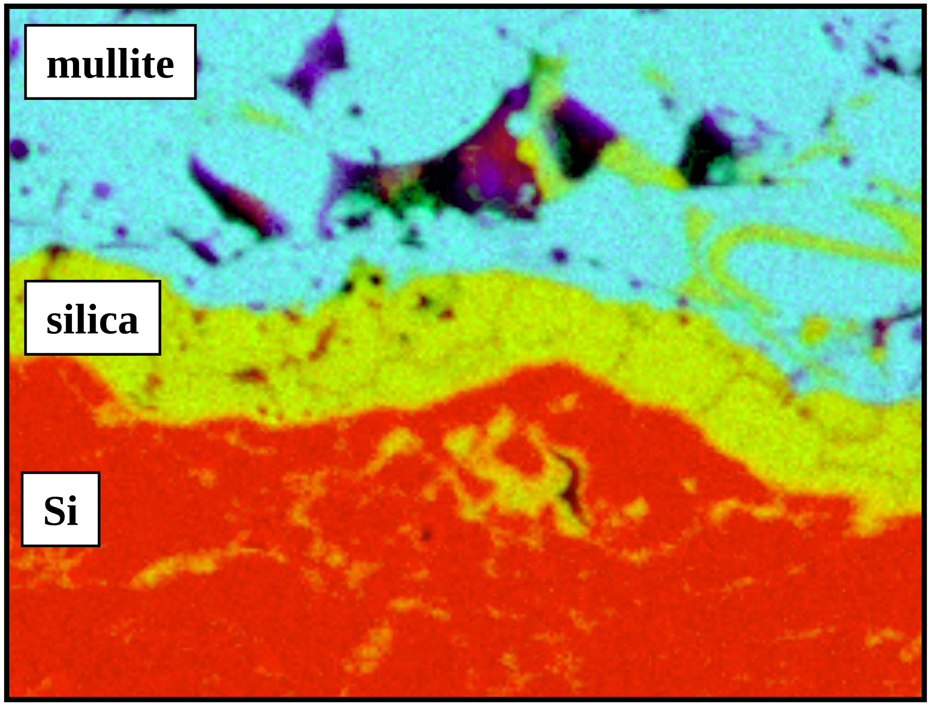
Poor Permeation Barrier

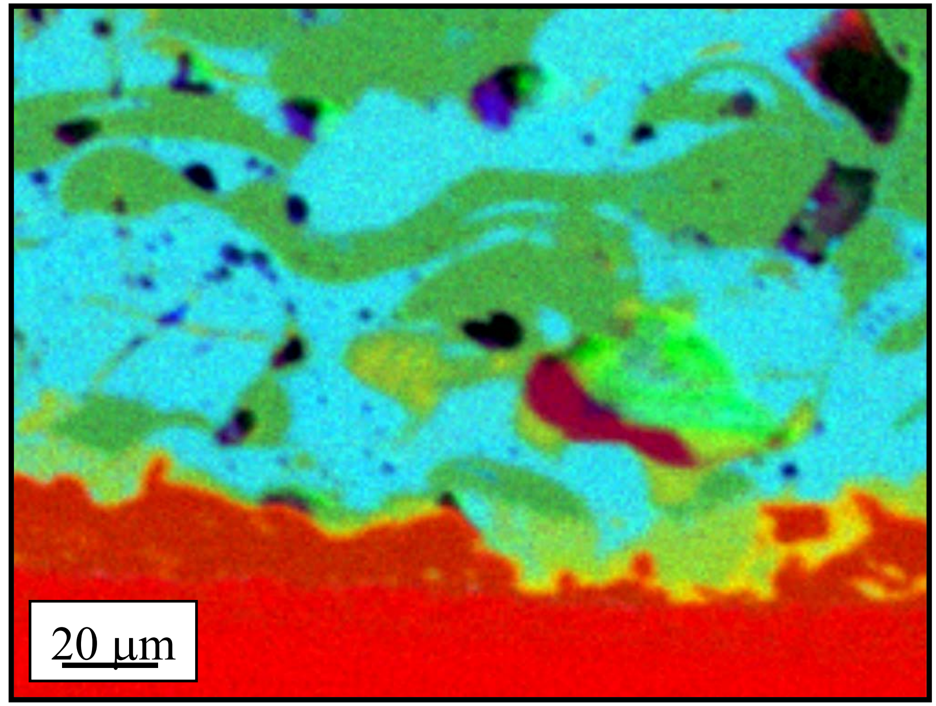
Oxidant Permeates Rapidly Through Coating And Substantial Substrate Oxidation Is Observed



Elemental Imaging Clearly Indicated The Difference In Amount Of Si Oxidation Under Different Coatings



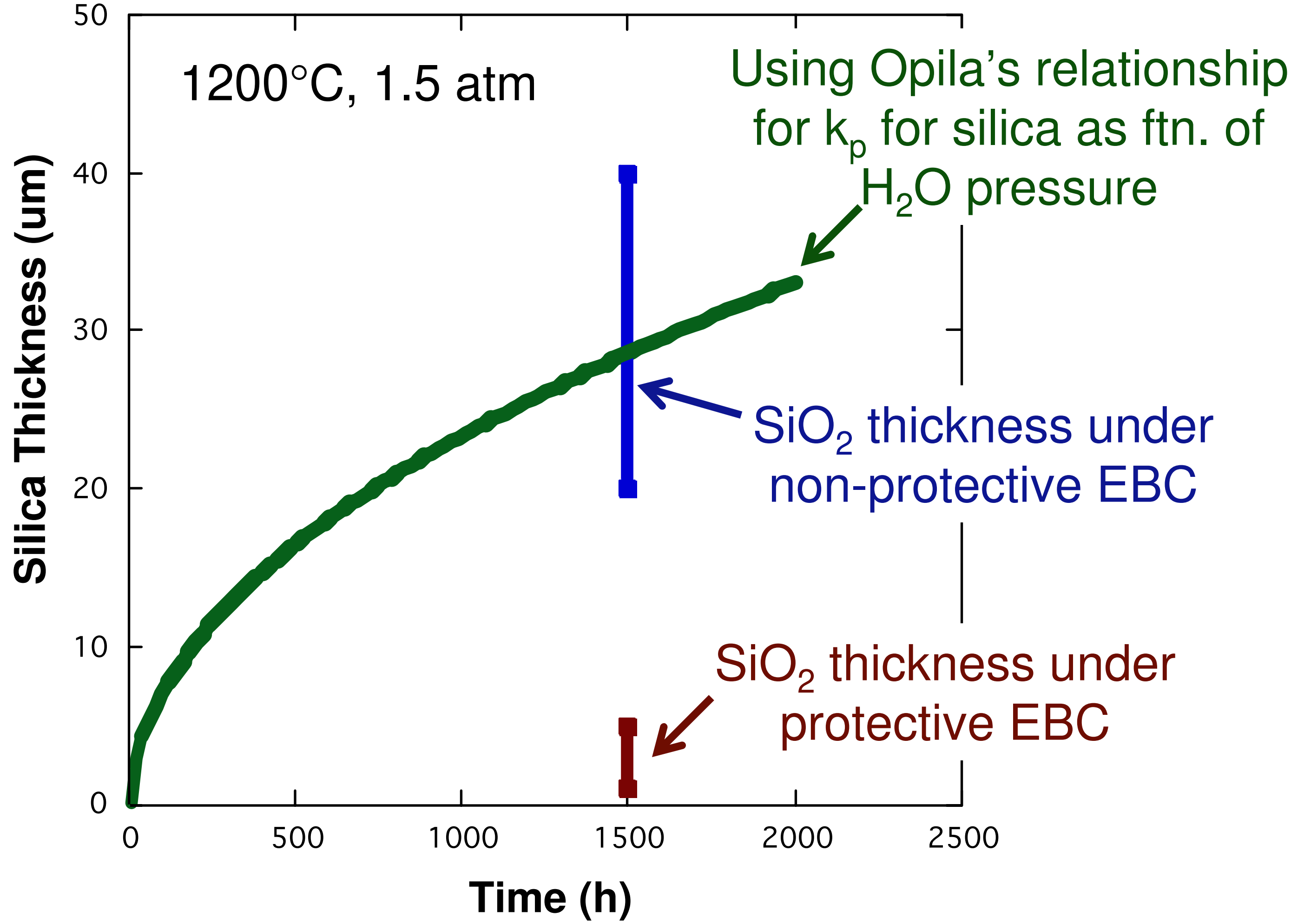
"Dual layer": Mullite/BSAS



"Mixed layer": (Mullite+BSAS)/BSAS

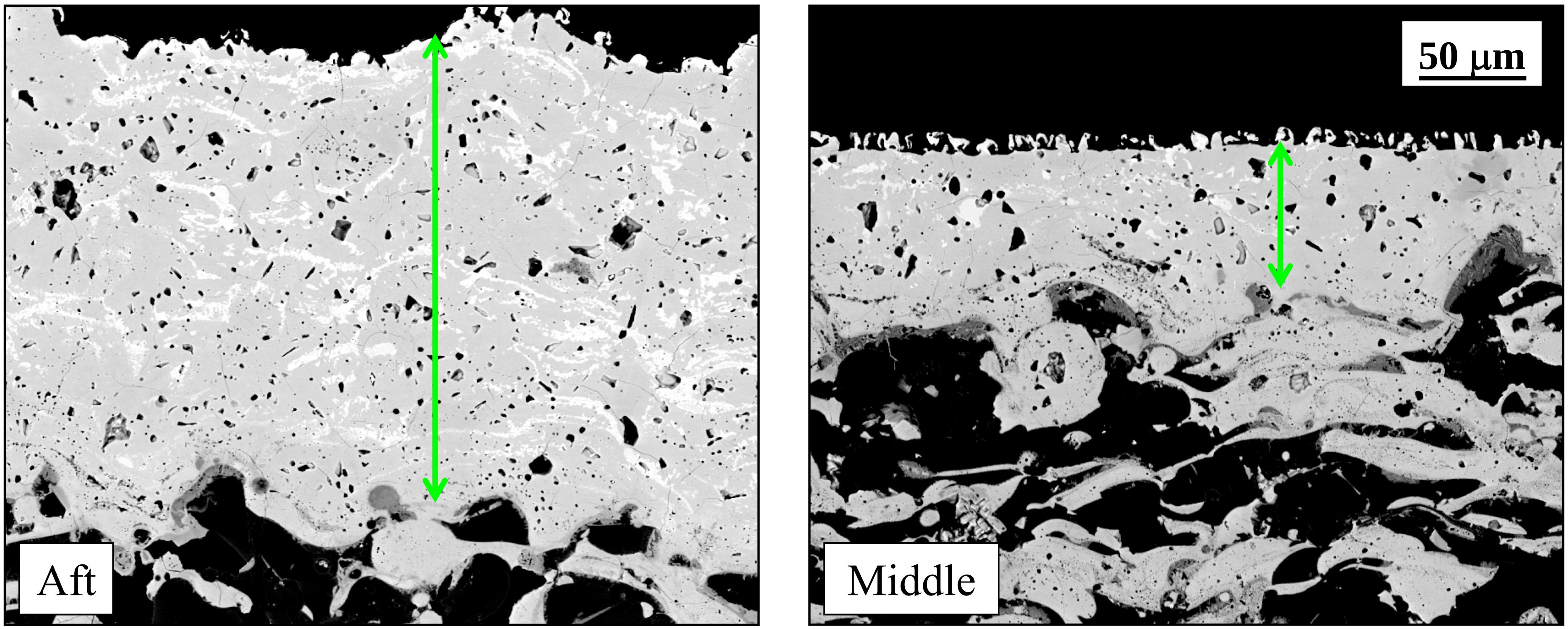
1500 h, 1200°C, 1.5 atm H_2O

Silica Thickness Data (Below EBC) Following Exposure Provides An Excellent Measure Of An EBCs Permeation Resistance



Volatilization In Combustion Environments Can Be Severe

- High oxidizing potential (H_2O pressure)
- High temperature
- High gas velocities



BSAS on SiC/SiC CFCC Combustor Liner
~14,000 h, 1.5 atm H_2O, 35 m/s, 1000-1200°C

We Have Recently Emphasized Use Of Very High H_2O Pressures To Assess Volatilization Susceptibility

- Thermal stability
- Possible interactions with substrate
- Ability to function as a permeation barrier to oxidizing species

10 atm total pressure
1-2 atm H_2O

- Volatilization resistance → 20 atm total pressure ~18 atm H_2O

➢ GT2004-53863: theoretical basis
➢ GT2005-69064: experimental results (proof of principle)

It Is Based On Compensating For Low Gas-Flow Velocities In Our Rigs By Increasing H_2O Pressure

Mass flux of volatile species, $A_yO_{x+z}H_{2x}$

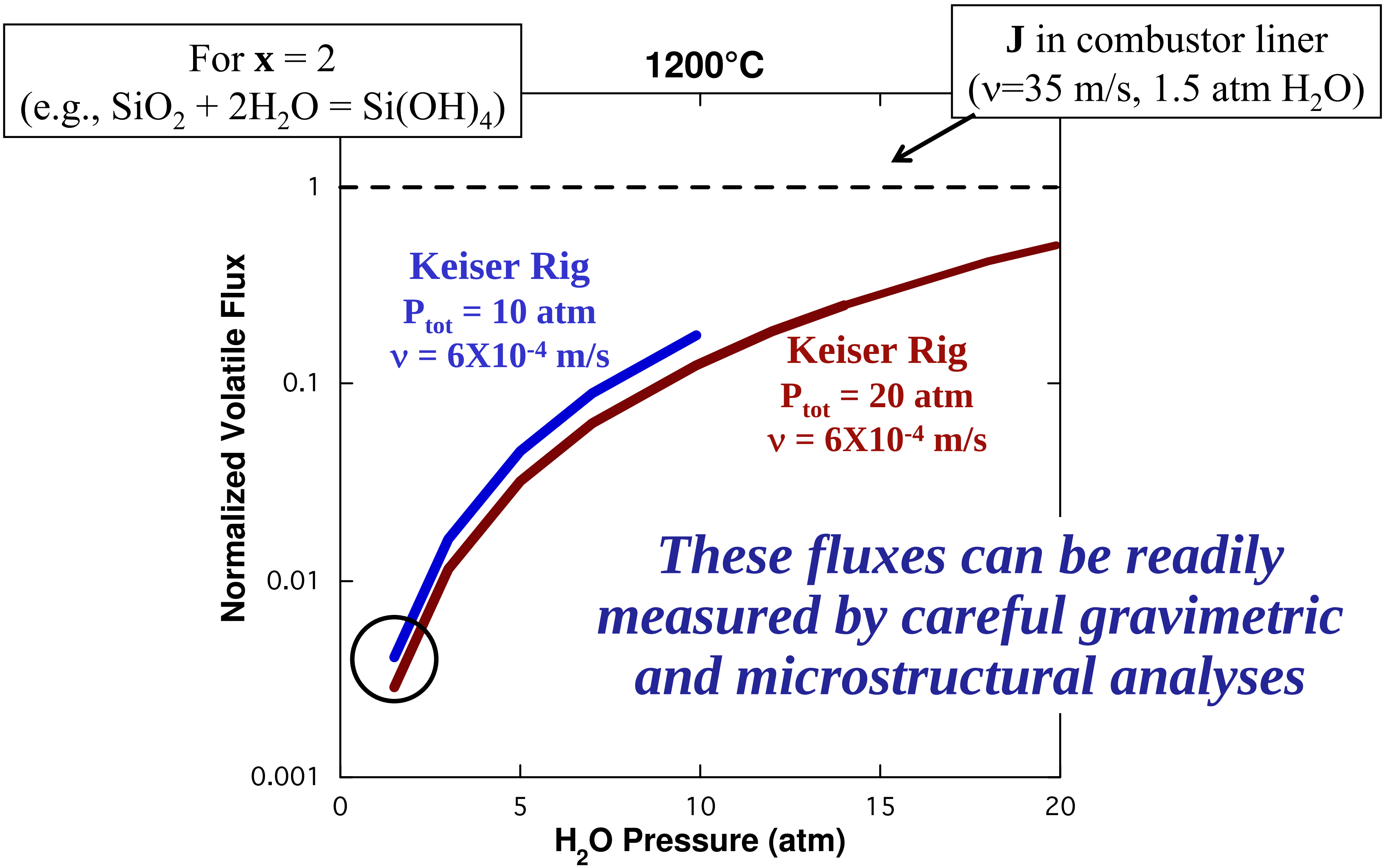
$$v^{0.5} \cdot \exp(-\Delta G/RT) \cdot P_{H_2O}^{x} / \sqrt{P_{tot}}$$

gas velocity

total pressure

Potential for providing simplified, but effective initial screening of volatilization susceptibilities of certain candidate EBCs in water vapor (in addition to permeability, and thermal, interfacial stability)

Substantial Volatile Fluxes Can Be Obtained In This Manner



These fluxes can be readily measured by careful gravimetric and microstructural analyses

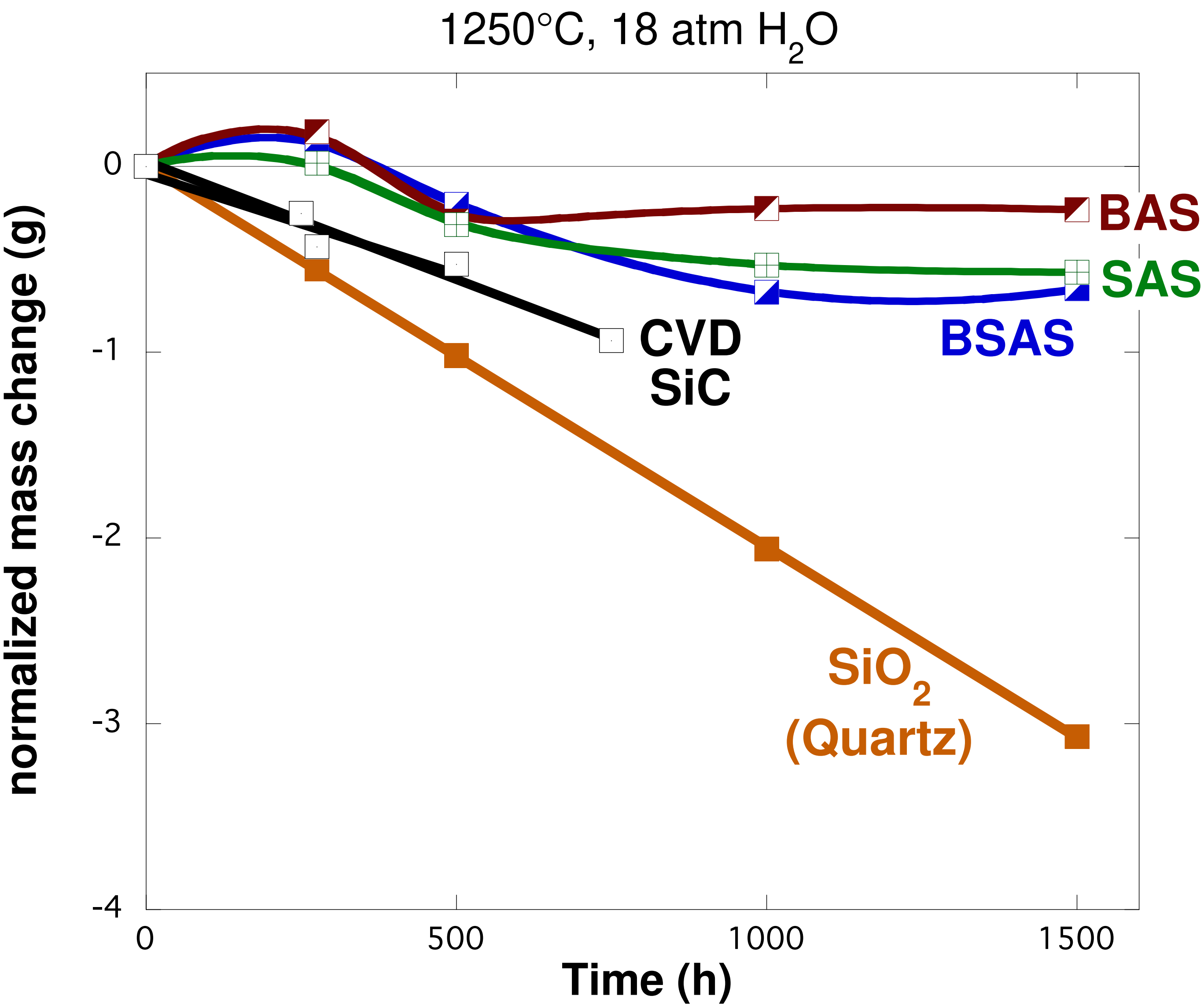
Initial Experimental Approach

- Bulk specimens
  - SiO_2 (baseline)
  - CVD SiC
  - $BaO-Al_2O_3-SiO_2$ (BAS)
  - $SrO-Al_2O_3-SiO_2$ (SAS)
  - $BaO-SrO-Al_2O_3-SiO_2$ (BSAS)

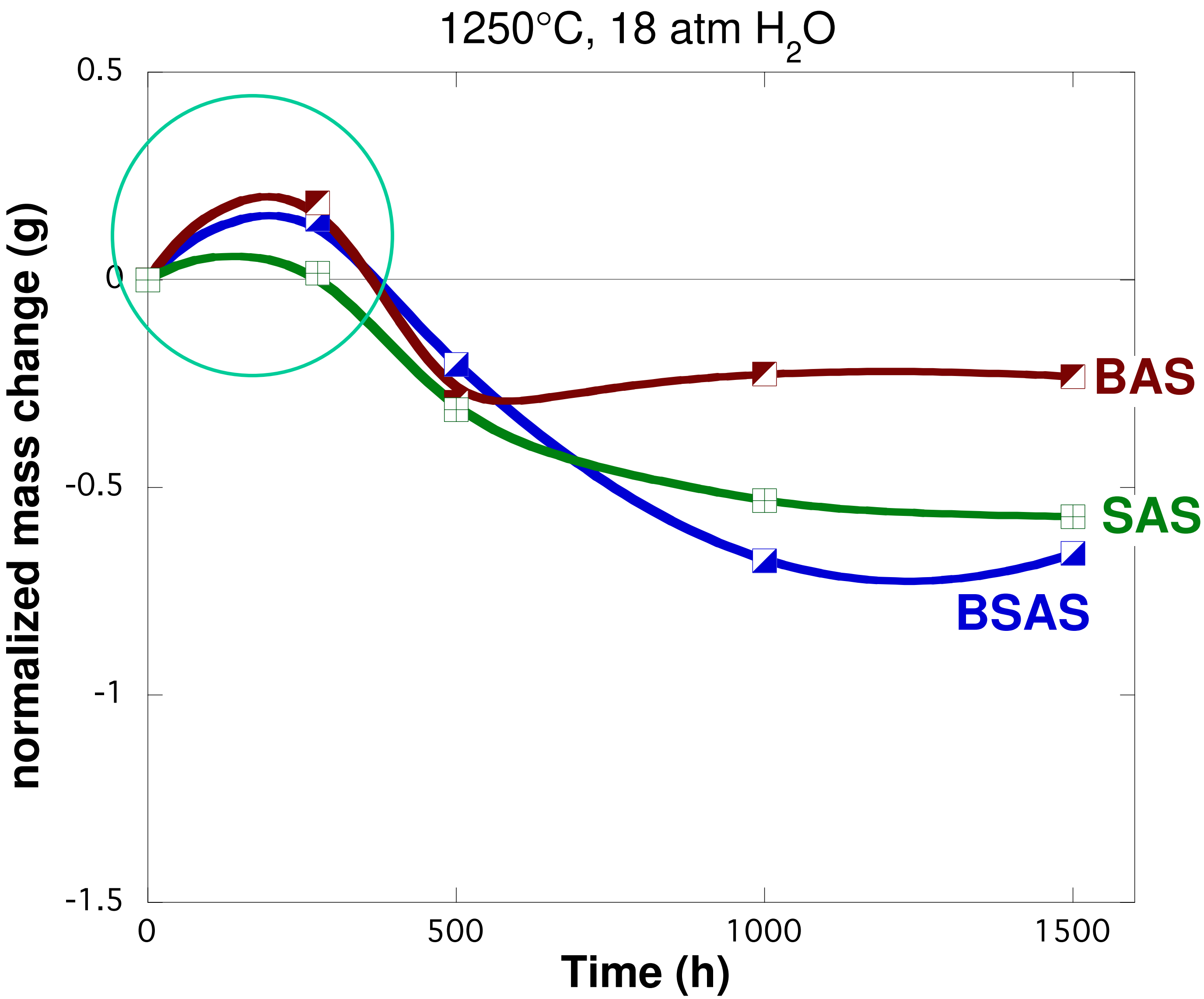
- 1250°C, 18 atm H_2O, 500-h intervals

- Post-exposure evaluation
  - Mass changes
  - Microstructural analysis

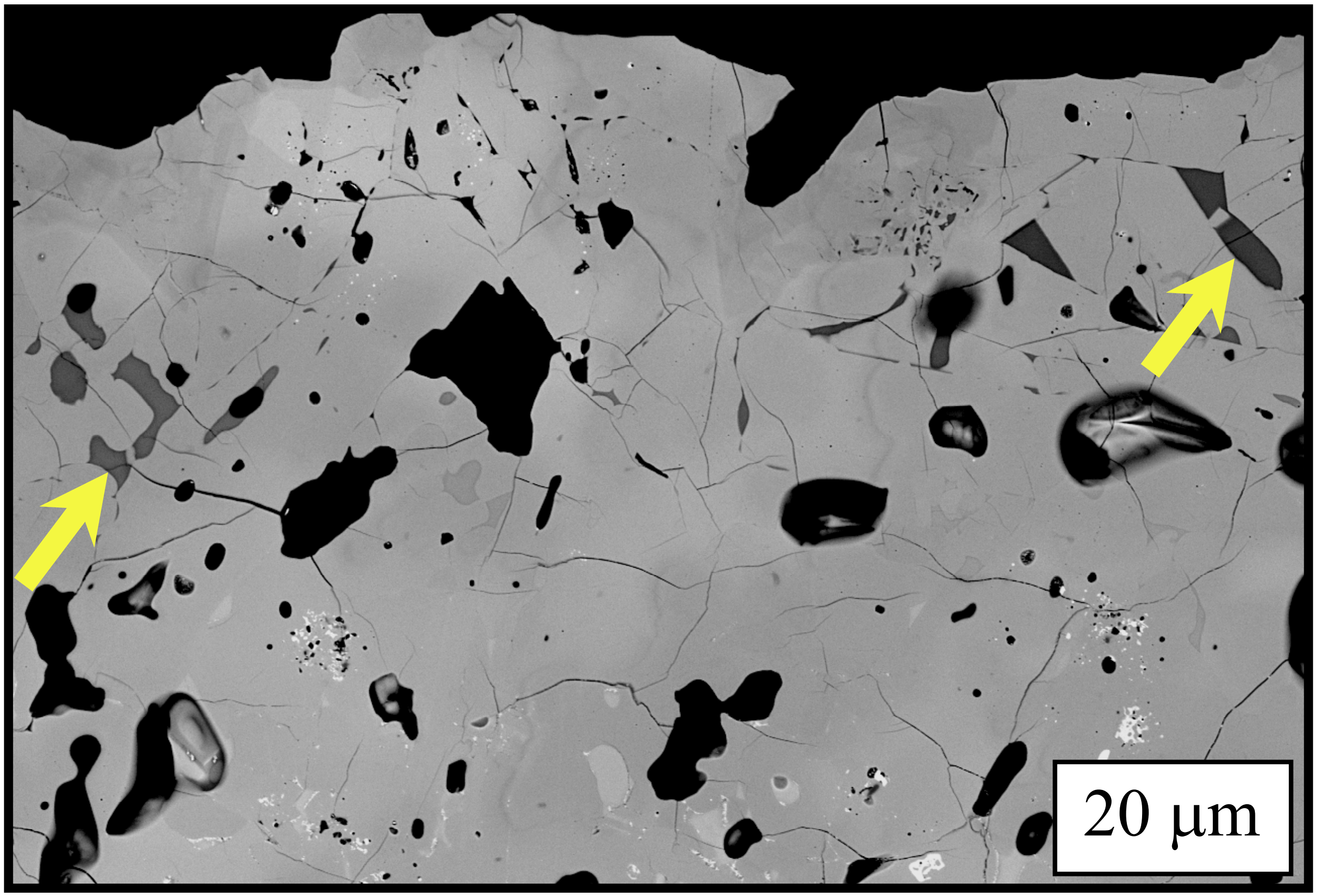
Our Initial Experimental Results Qualitatively Confirmed Prediction



Phase Rearrangement May Be Prerequisite For Onset Of Net Mass Loss

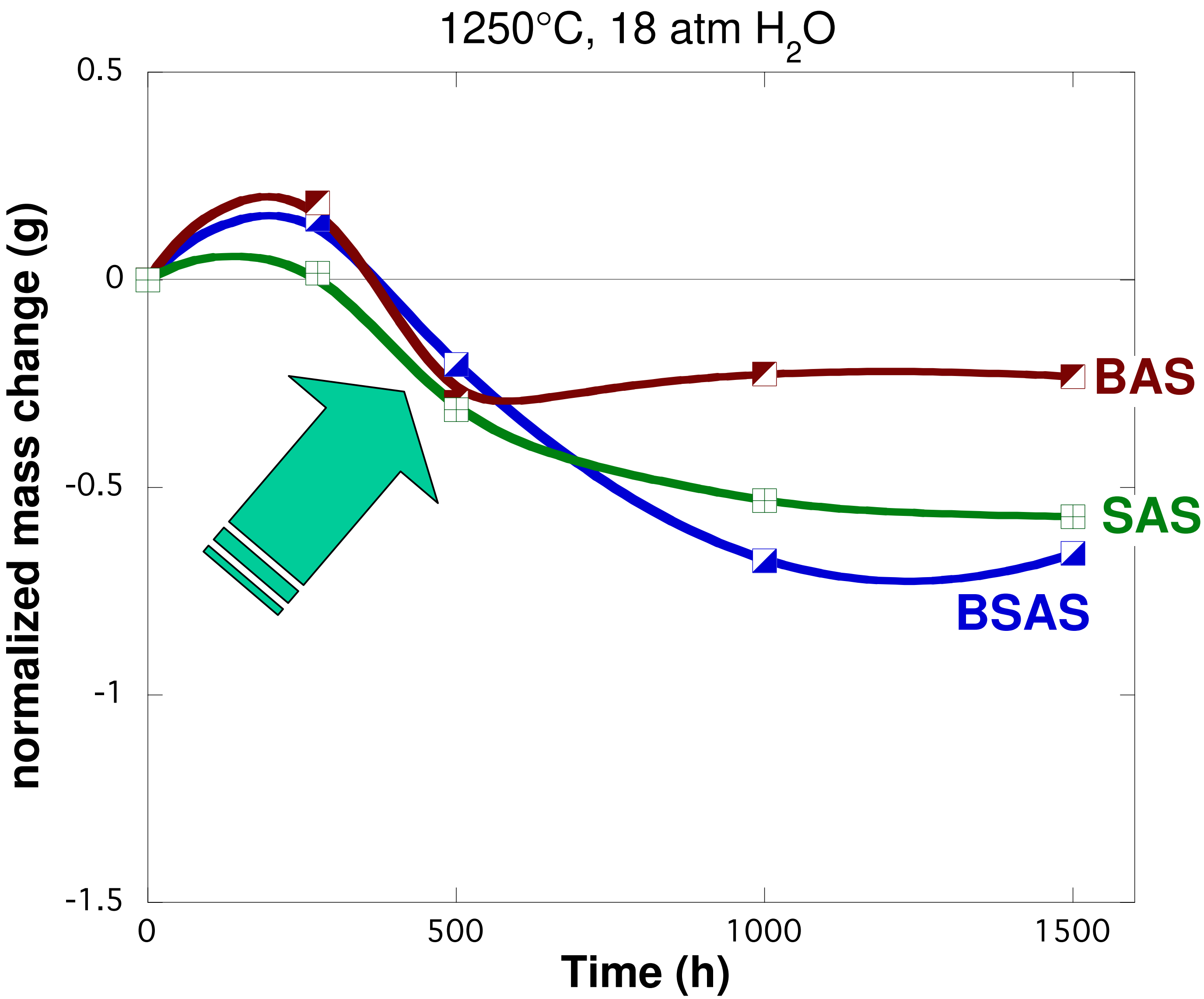


Microstructural Analysis Revealed Phase Separation Of SiO_2-Rich Constituent After 500 h

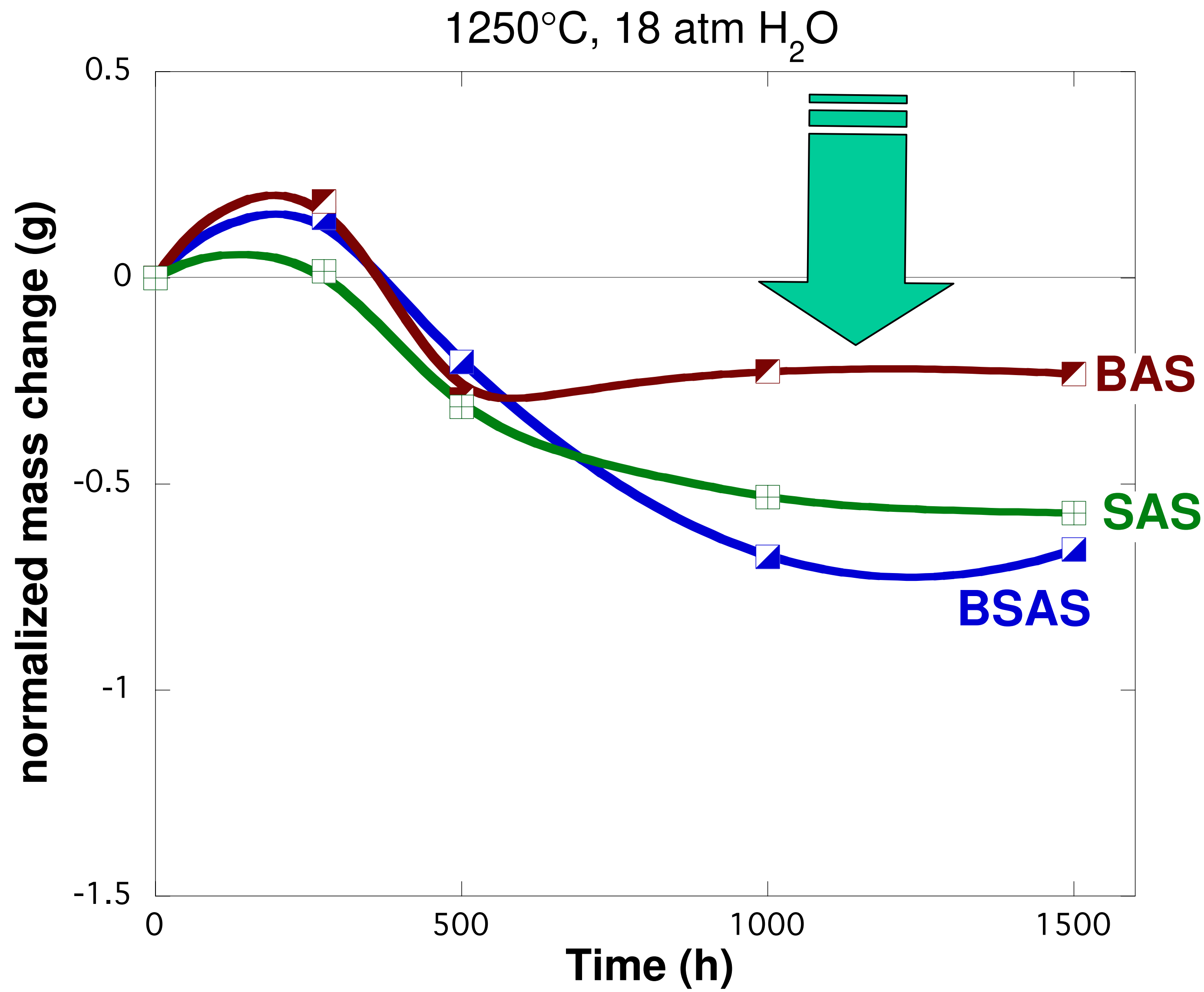


BAS, 1250°C, 500 h, 18 atm H_2O

Mass-Loss Stage Would Be Consistent With Volatilization Of SiO_2-Rich Phase

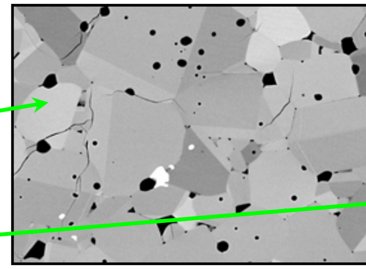


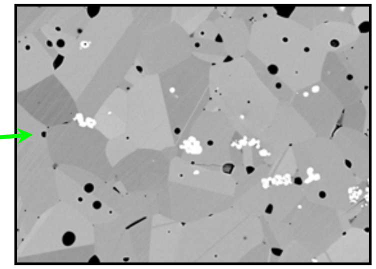
If Phase Separation Sluggish Relative To Volatility, Rate Of Mass Loss Should Decrease With Time

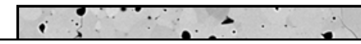


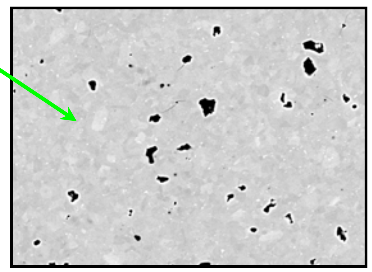
Stand-Alone EBC Compositions And EBCs On Si-Based Substrates Are Currently Being Exposed

- Bulk specimens
  - $Lu_2Si_2O_7$
  - $Yb_2Si_2O_7$
  - $Y_2Si_2O_7$
  - $SrAl_2Si_2O_7$
  - BSAS





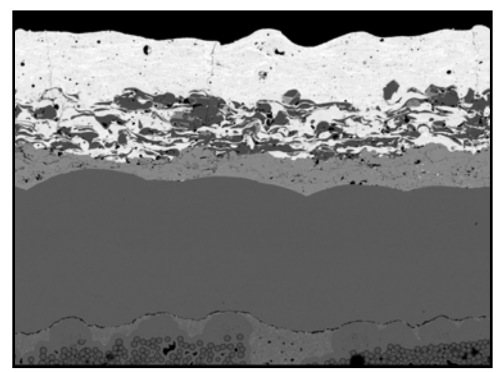




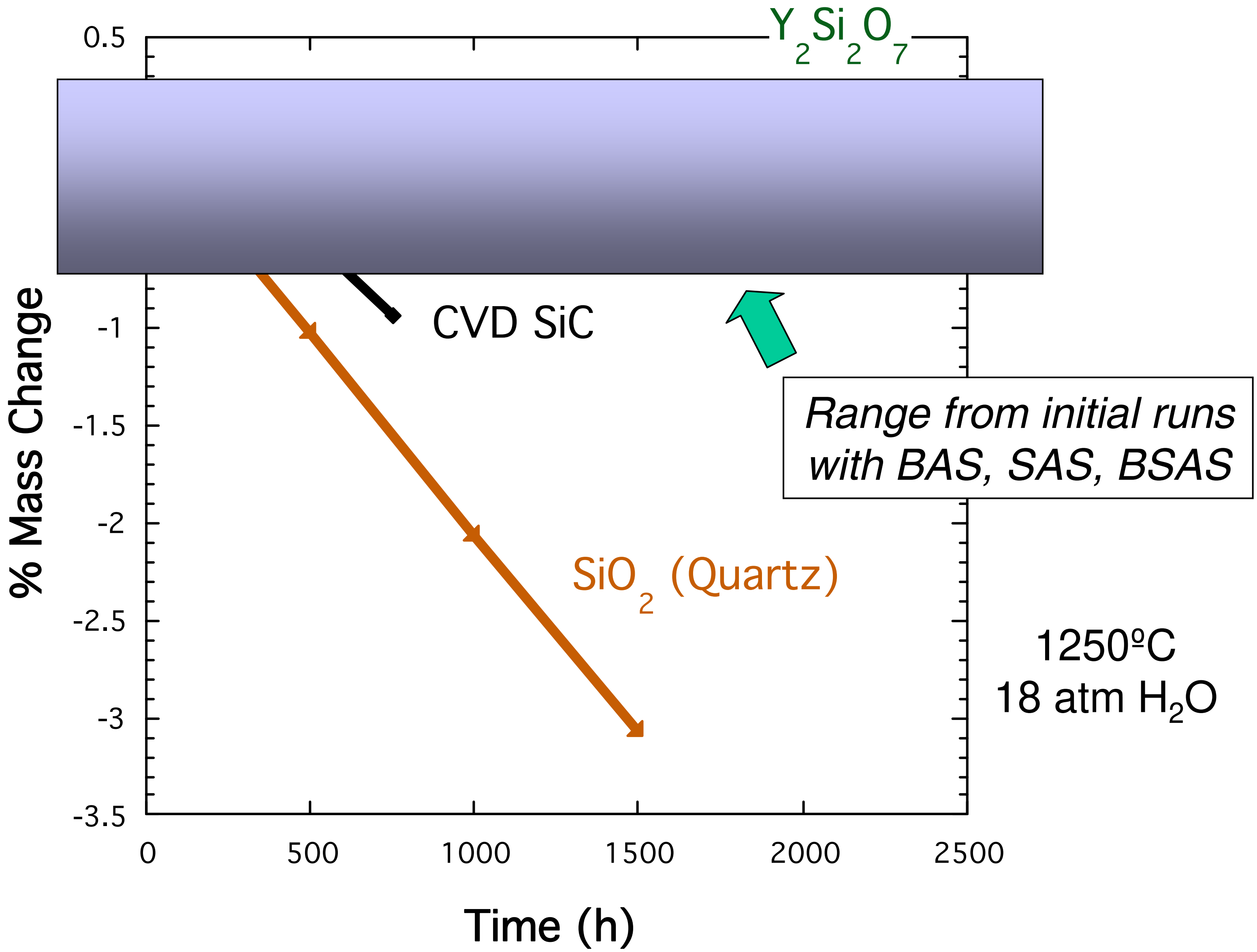
34 EBC Formulations,
7 standards,
Over 40,000 specimen-h
at 1250ºC, 18 atm H_2O

- Numerous Proprietary Compositions

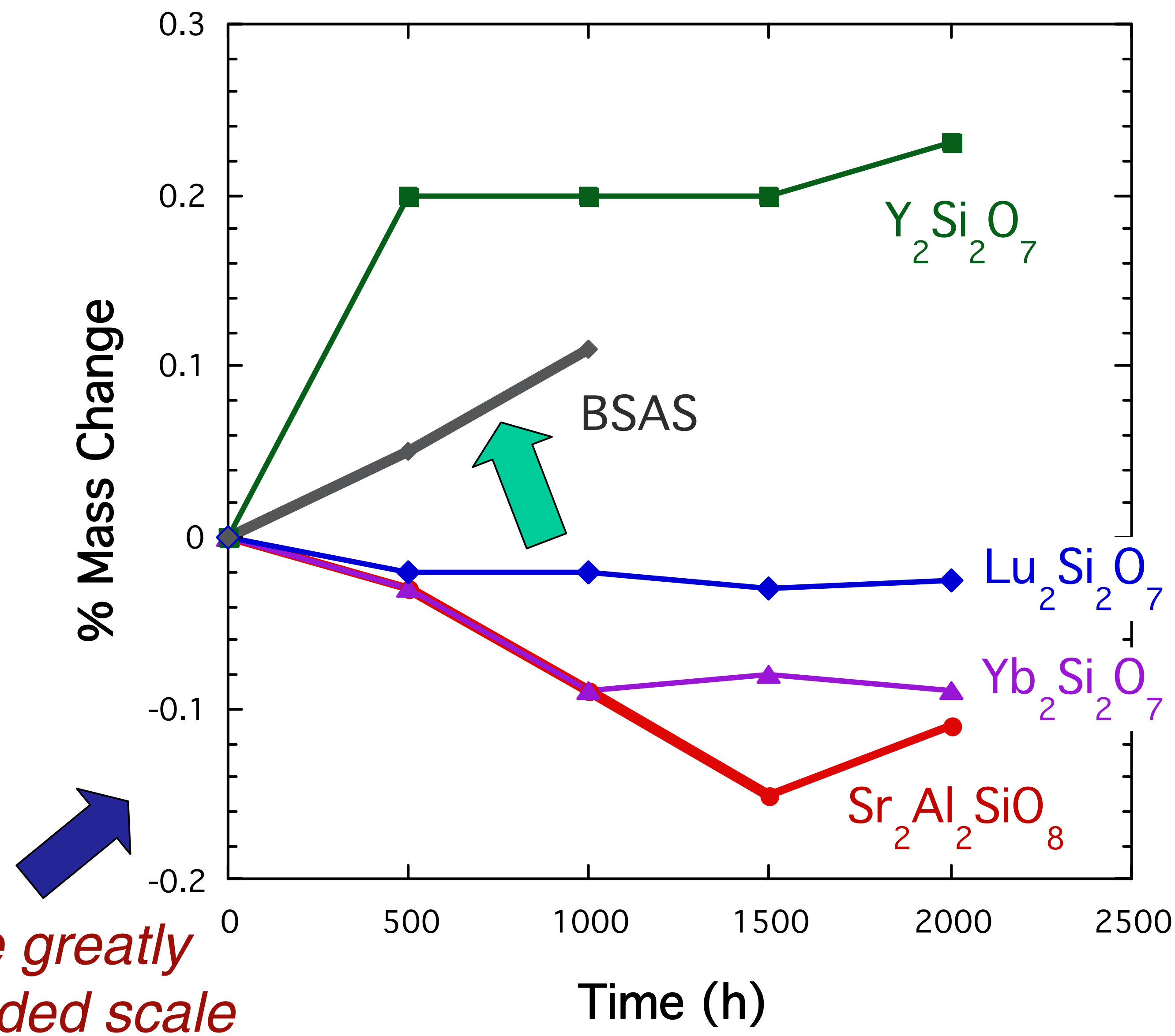
- SAS, BSAS on CFCC substrates



Bulk Silicates Prepared At ORNL By Steve Nunn Showed Good Volatilization Resistance

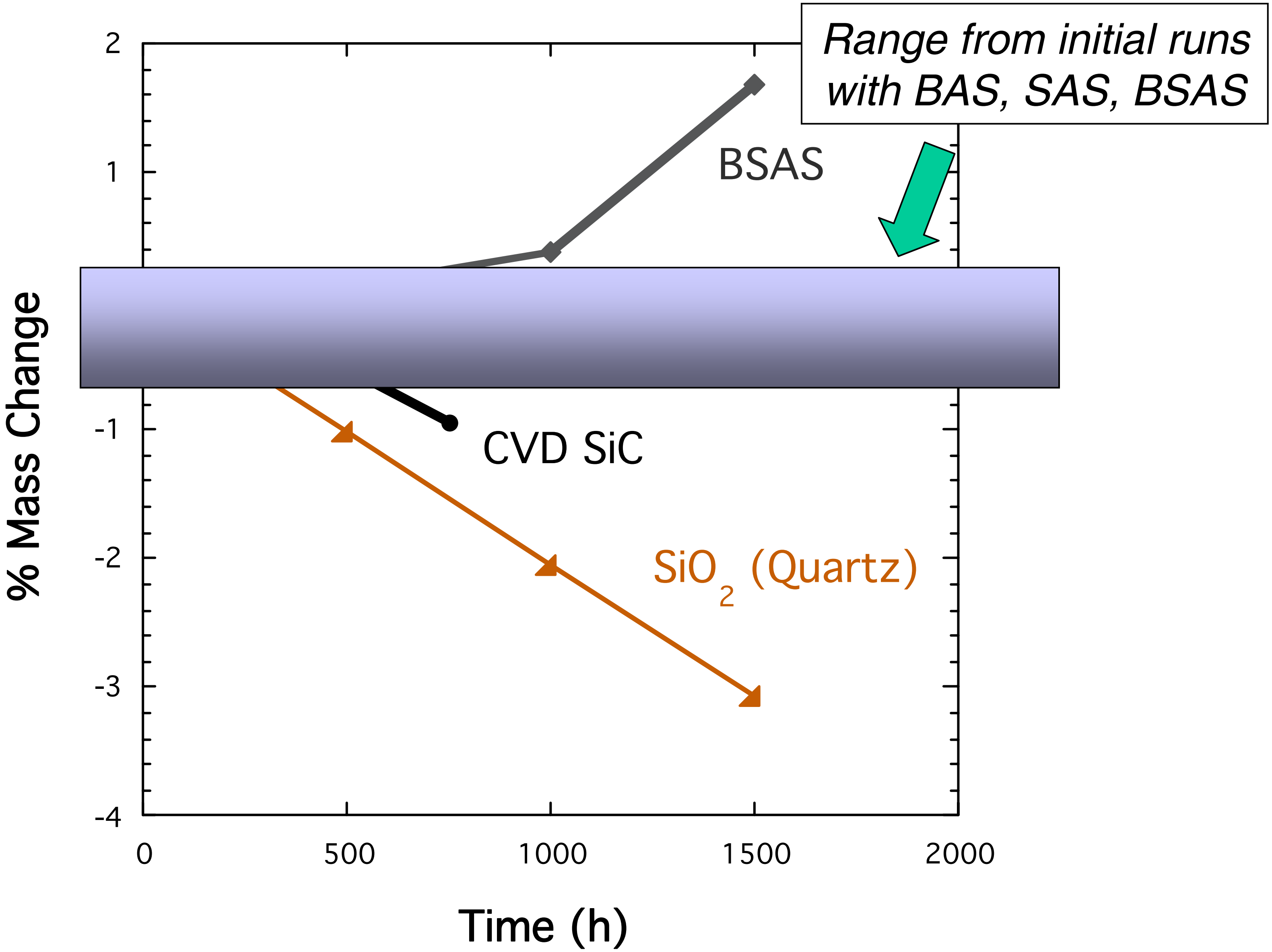


New Bulk BSAS Fell Within This Narrow Range Of Mass Change



Note greatly expanded scale

But Other Bulk BSAS Behaved Somewhat Differently



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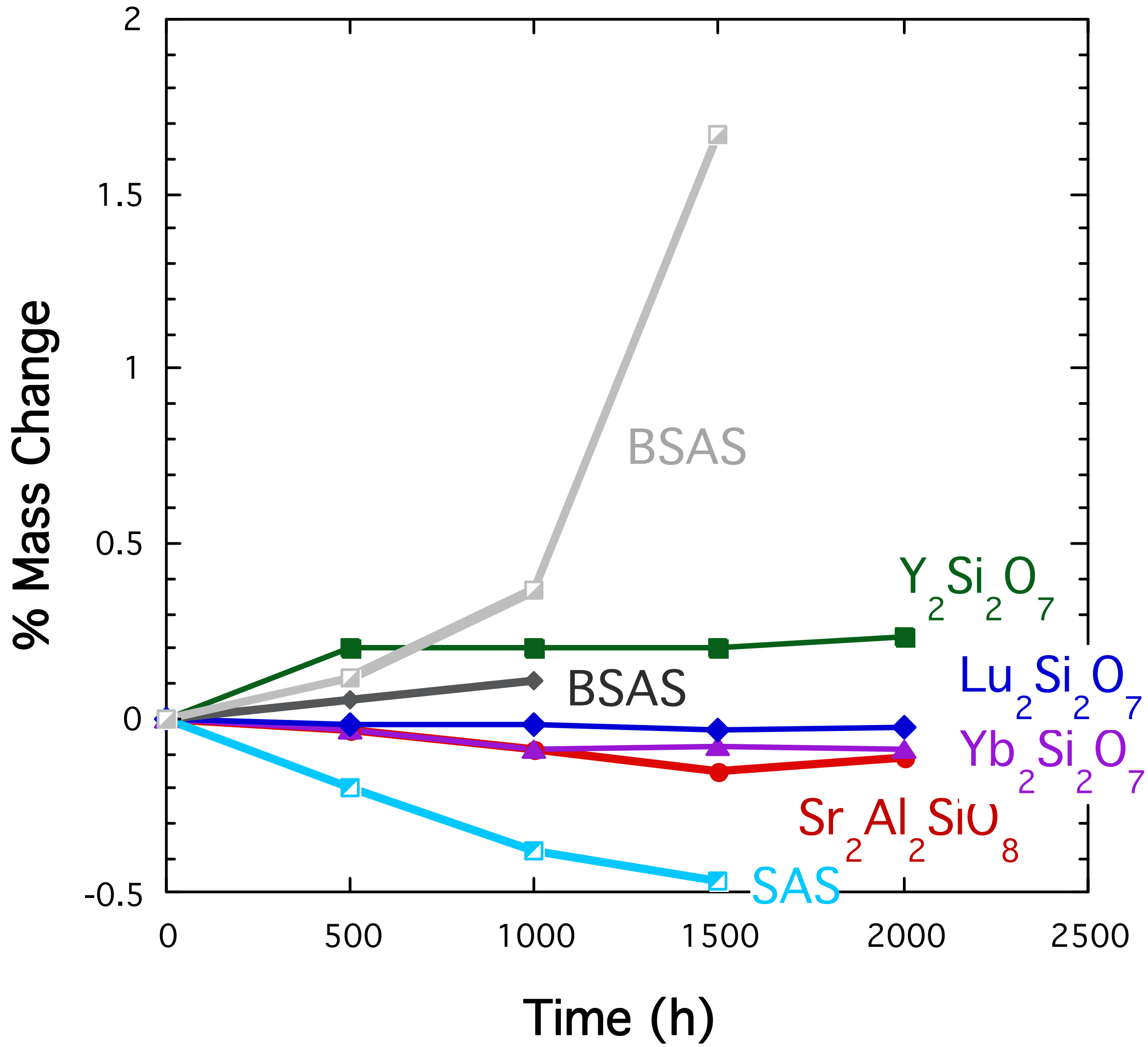
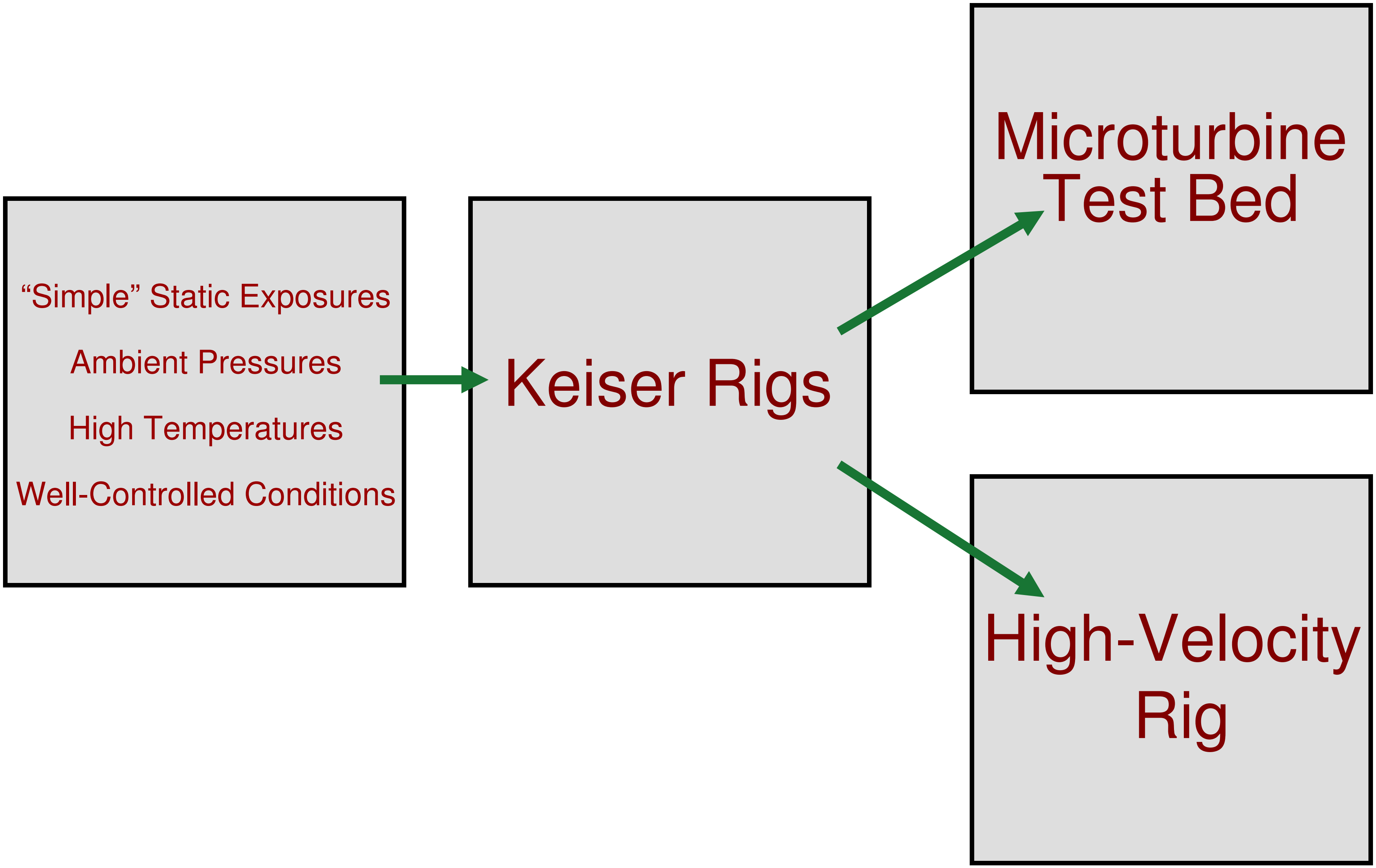


This Type Of Exposure Provides Intermediate Step; Prototypic Tests Needed For Most Promising Mat'ls.



Summary

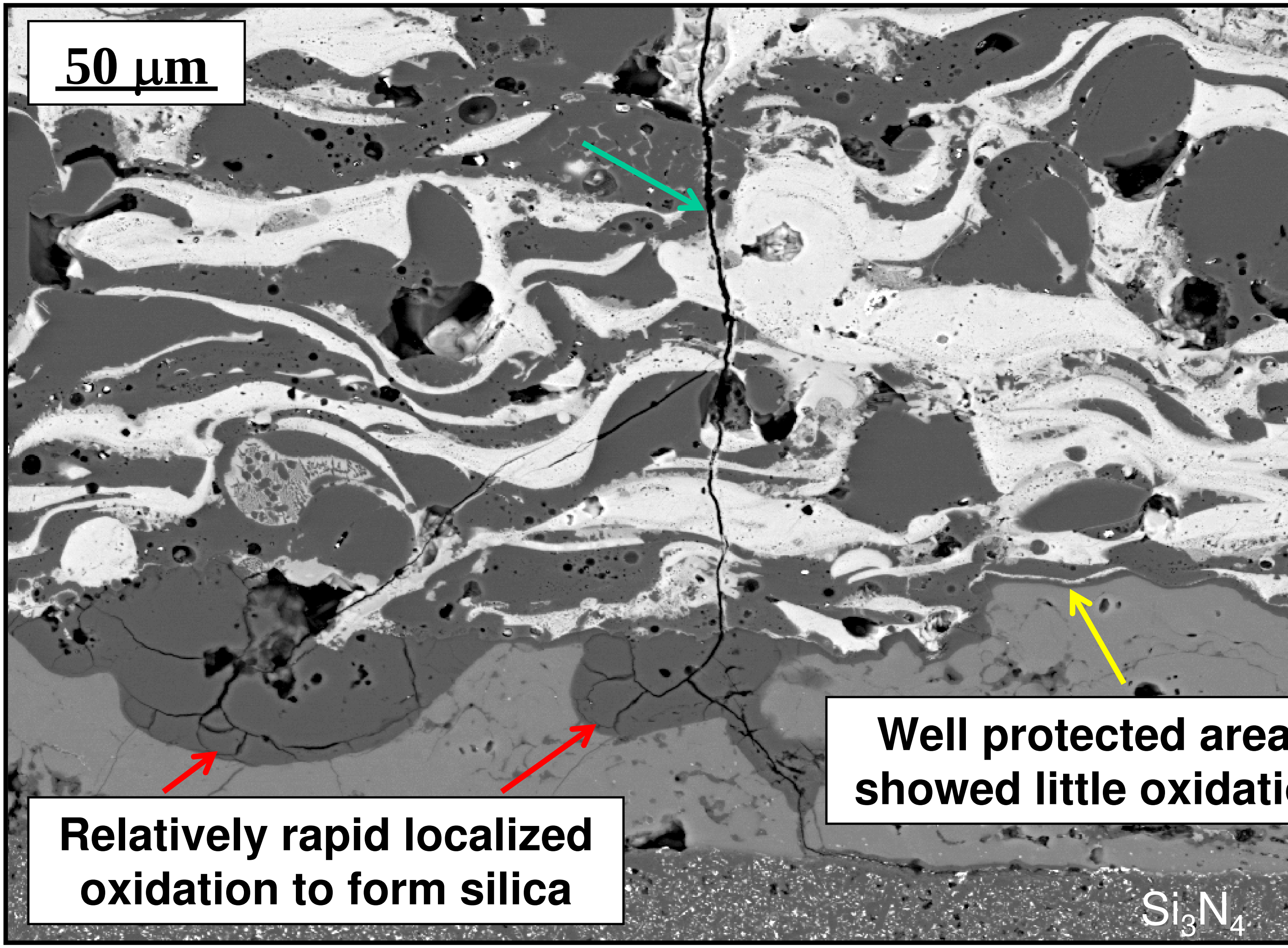
- Recent results indicate that we can differentiate volatilization resistance among various candidate EBCs by conducting experiments at very high water vapor pressures (order of 20 atm)

- Microstructural characterization is needed to rigorously evaluate compositional/structural changes during high-temperature exposures at high water-vapor pressures

- Gravimetric results are useful in comparing rates relative to pure silica and in directly relating environmentally induced structural and chemical changes in the ceramic to effects on volatilization susceptibility

Extra Slides

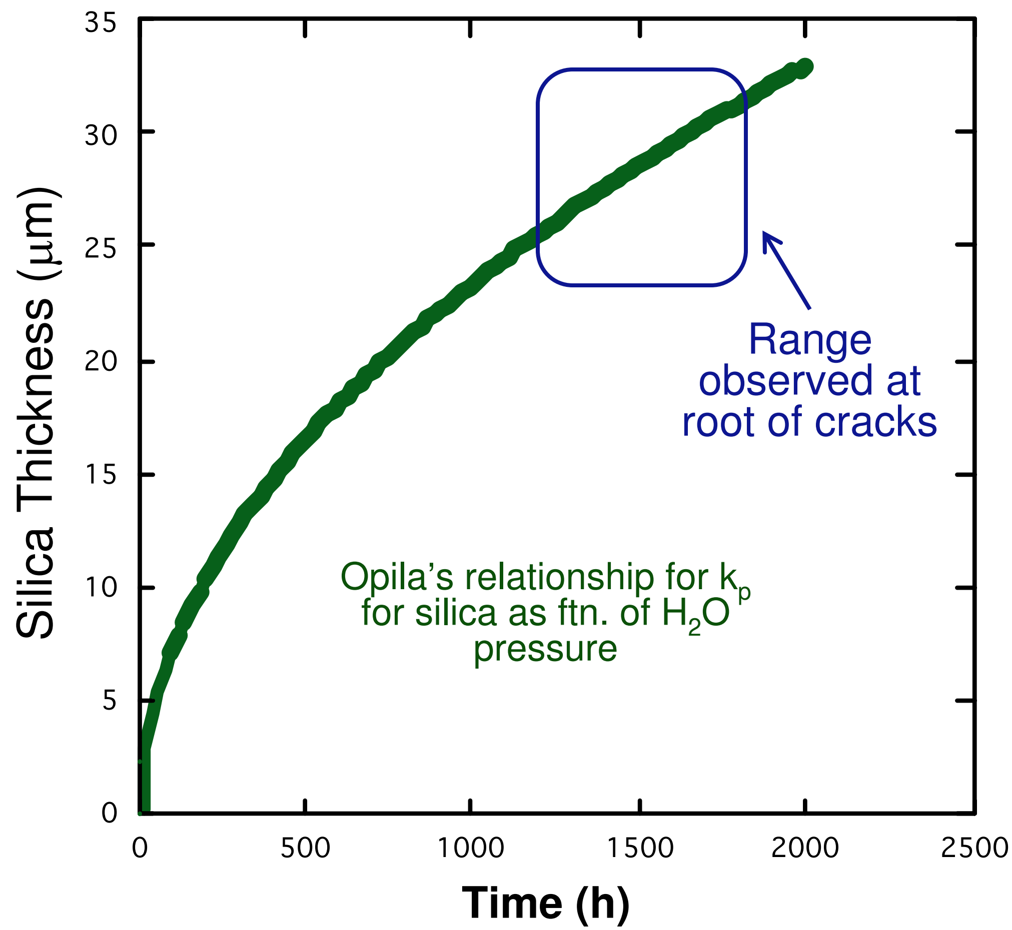
Isolated Through-Thickness Cracks Clearly Provide Paths For Oxidant Ingress



2000 h, 1200°C, 1.5 atm H_2O

Processing Defects Obviously Play A Critical Role In EBC's Protective Ability

- Inherent resistance to permeation can be seriously compromised by extended defects
- Cracks do not provide any resistance to oxidant transport - in most cases, volume of silica at roots of cracks similar in extent to what's expected for uncoated Si-bearing materials in high-pressure water vapor

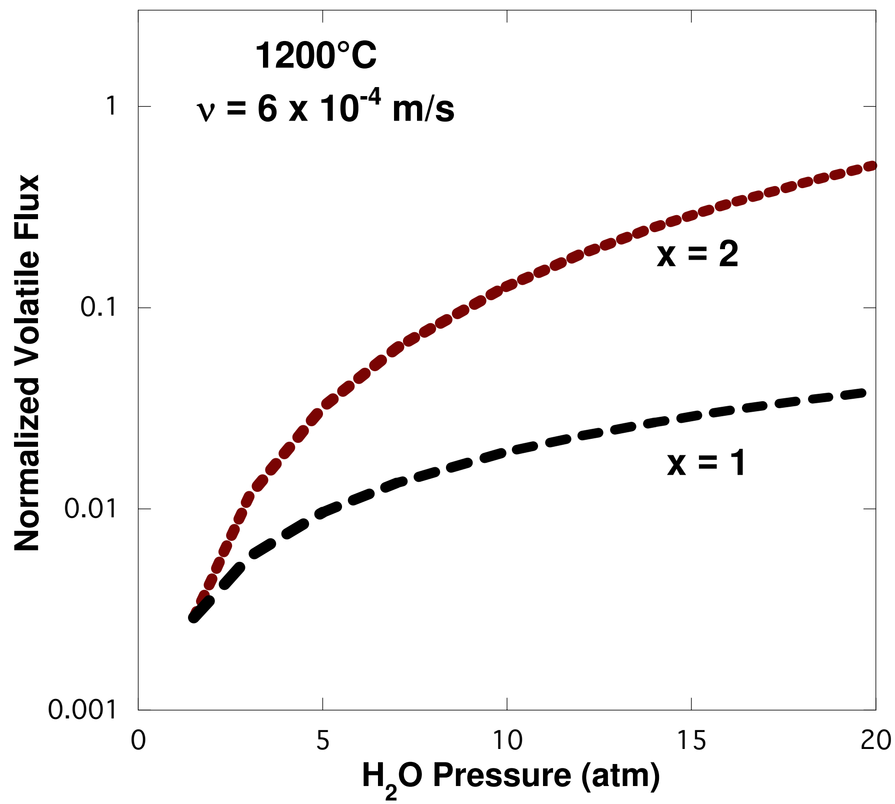


Utility Of Approach Dependent On Stoichiometry Of Volatile Species

$$A_yO_z\ (s) + xH_2O\ (g) = A_yO_{x+z}H_{2x}\ (g)$$

$$\text{Flux: } v^{0.5} \bullet \exp\left(-\Delta G/RT\right) \bullet P_{H_2O}^{x}/\sqrt{P}_{tot}$$

Volatilization rate scales with water-vapor pressure to the x power:



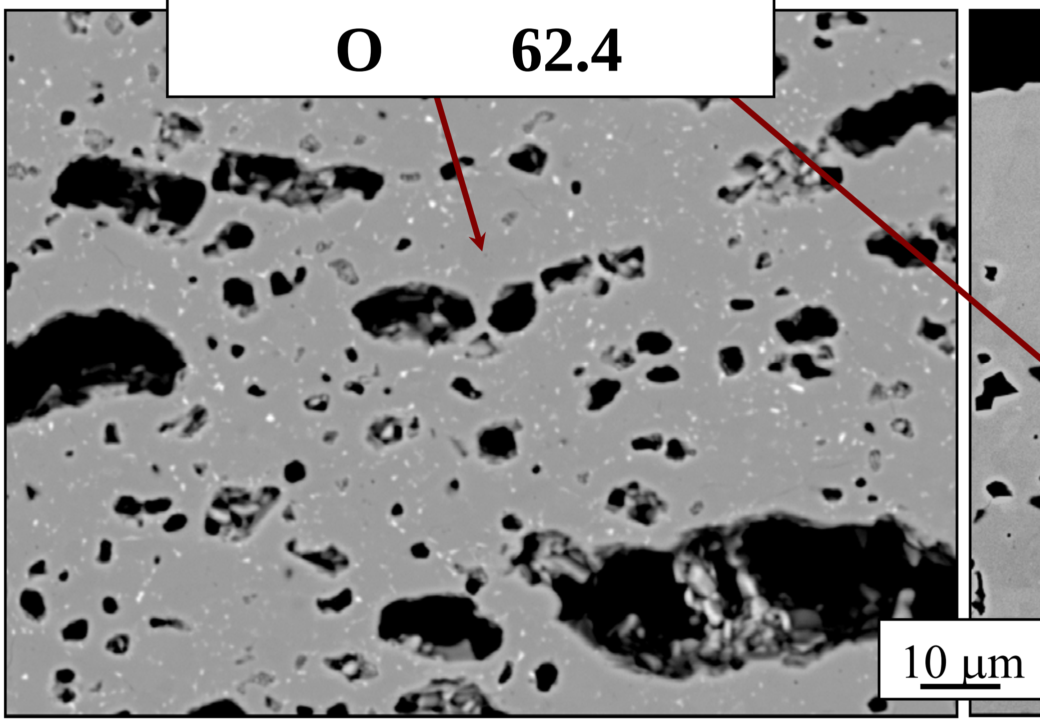
Implications Of Dependence Of Volatilization Rate On x

- Experimental approach of increasing water-vapor pressure is more effective for solids that require more moles of water to form a mole of volatile product - for example, silica forming $Si(OH)_4$
- This factor must be considered when comparing results among different types of compositions

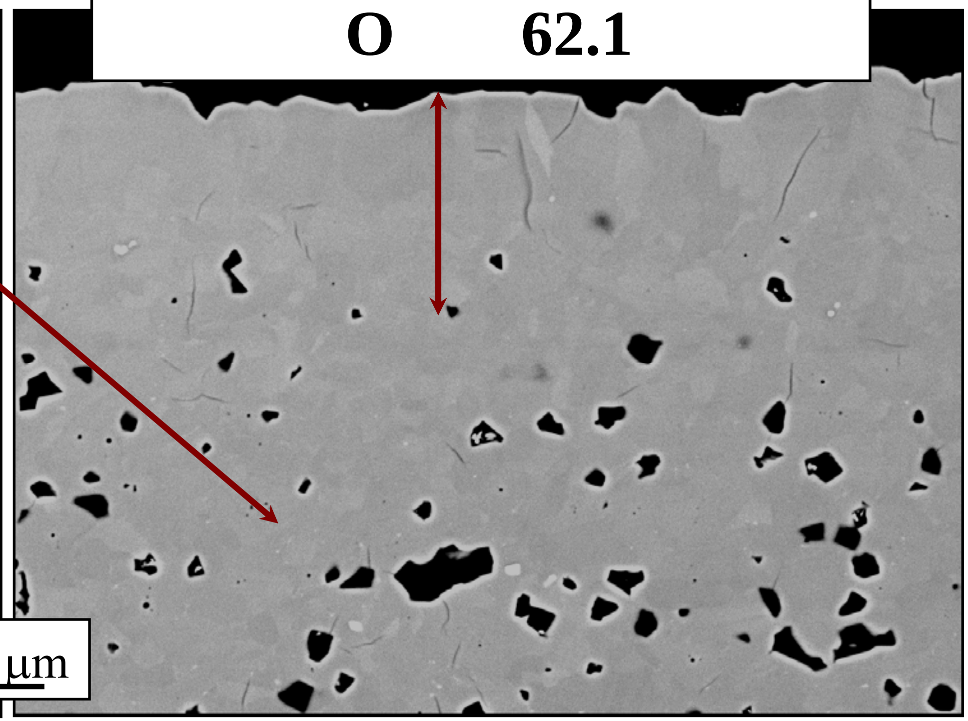
Consistent With Delay In Mass Loss, No Apparent Depletion Of Silica Was Observed After First 500 h

Matrix comp. (at.%)	
Sr	7.6
Al	15.0
Si	15.0
O	62.4

Surface layer comp. (at.%)	
Sr	7.6
Al	15.0
Si	15.3
O	62.1



As-processed microstructure

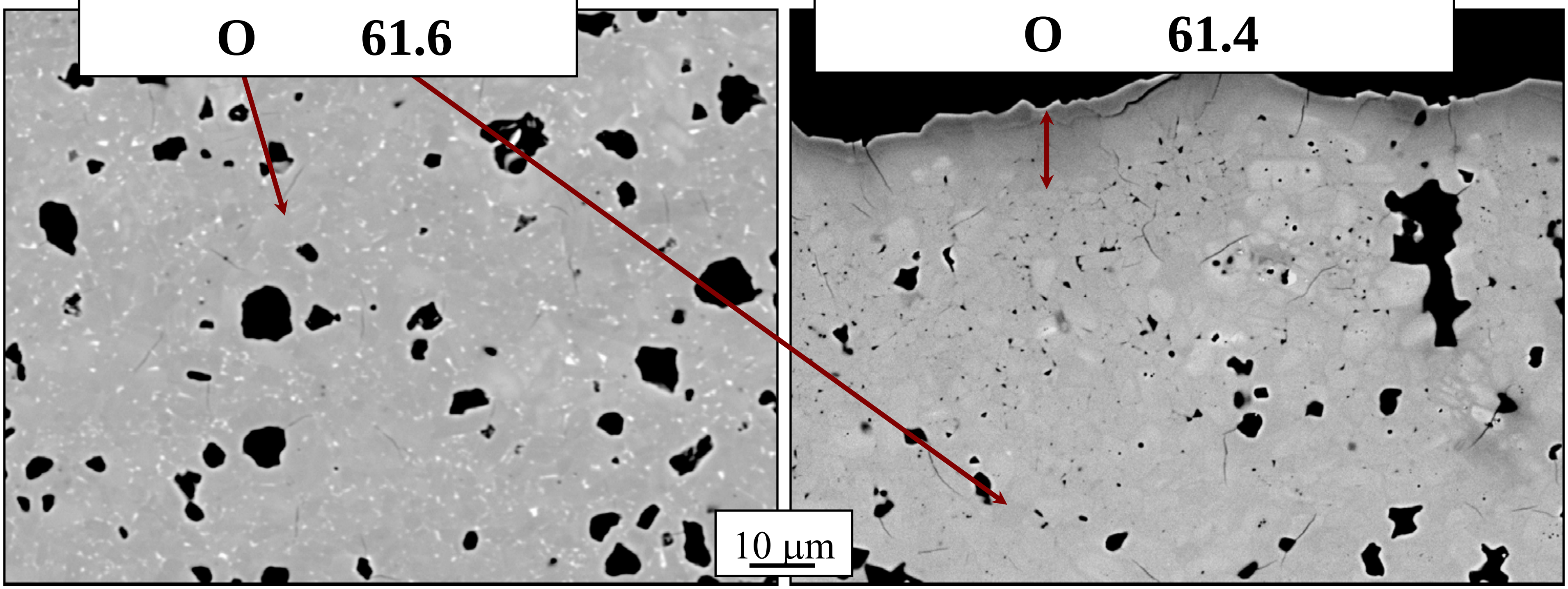


SAS surface after 500 h

Consistent With Delay In Mass Loss, No Apparent Depletion Of Silica Was Observed After First 500 h

Matrix comp. (at.%)	
Ba	5.9
Sr	1.8
Al	15.4
Si	15.3
O	61.6

Surface layer comp. (at.%)	
Ba	3.5
Sr	3.7
Al	14.9
Si	16.4
O	61.4



As-processed microstructure

BSAS surface after 500 h